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Huangfu, Shangxiong ; Zhang, Xiaofu ; Schilling, Andreas

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DOI: <https://doi.org/10.1103/physrevresearch.2.033247>

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ZORA URL: <https://doi.org/10.5167/uzh-191275>

Journal Article

Published Version



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Originally published at:

Huangfu, Shangxiong; Zhang, Xiaofu; Schilling, Andreas (2020). Correlation between the tolerance factor and phase transition in $A_{4-x}B_xNi_3O_{10}$ (A and B=La,Pr,and Nd;x=0,1,2,and 3). *Physical review research*, 2(3):033247.

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Correlation between the tolerance factor and phase transition in $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$; $x = 0, 1, 2$, and 3)

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(Received 17 March 2020; accepted 6 July 2020; published 13 August 2020)

We have synthesized a series of the Ruddlesden-Popper nickelate solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$; $x = 0, 1, 2$, and 3) via the citrate precursor method in different reacting atmospheres. Both the electronic-transport and magnetization measurements on these samples show well-defined phase transitions at temperatures between 135 and 165 K. These transition temperatures as well as the room-temperature resistivities strongly correlate with the Goldschmidt tolerance factor t , irrespective of the combination of the magnetic rare-earth ions with nonmagnetic La^{3+} . We conclude that these changes of the electronic properties are mostly a consequence of the distortion of the NiO_6 octahedra at the phase transition which is intimately related to the tolerance factor t , but appear to be rather insensitive to the average magnetic moment of the rare-earth ions upon exchanging La by Pr or Nd.

DOI: [10.1103/PhysRevResearch.2.033247](https://doi.org/10.1103/PhysRevResearch.2.033247)

I. INTRODUCTION

Due to the strongly correlated d -electrons, some layered transition-metal oxides give rise to various phases with different intriguing electronic and magnetic properties [1–4]. The transitions between these phases, e.g., metal-insulator transitions [5,6], paramagnetic-ferromagnetic transitions [7], or Mott-insulator-superconductor transitions [8–10], are driven by various parameters such as temperature, pressure, electric current, magnetic field, chemical composition, etc. [5,8,11–14]. Generally, these phase transitions are associated with distinct changes of the physical properties, such as heat capacity, resistivity, or magnetization. The Ruddlesden-Popper (RP) nickelates $A_{n+1}\text{Ni}_n\text{O}_{3n+1}$ are constituted by perovskite like structures piled by a number (n) of infinite NiO_6 -octahedron-based layers, allowing for many different species at the A site (rare-earth metals, La, Pr, and Nd, and alkaline metals such as Sr and Ba). Therefore, one may expect that there are many variants of distorted NiO_6 octahedra and tunable mixed-valence states of nickel with values between +2 and +3 in this series of compounds. Due to the diverse d -orbital states of the nickel ions, which in turn may lead to a variety of interesting physical phenomena, these RP nickelates have recently gained intensive attention.

By doping or substituting, the RP rare-earth nickelates show abundant and tunable physical properties and phase changes. The La^{3+} ions in La_2NiO_4 ($n = 1$), for instance, can be partially replaced by Ba^{2+} ions or Sr^{2+} ions. In the resulting solid solution of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, a maximum of the tetragonality ratio c/a is observed at $x = 0.5$ [15], and the semiconductor-metal crossover temperature monotonically decreases with increasing x from 0 to 1.2 [16], while

LaBaNiO_4 remains insulating down to the zero temperature, instead [17]. Moreover, the solid solution of $\text{LaSr}_{1-x}\text{Ba}_x\text{NiO}_4$ shows electronic-transport properties ranging from a metallic state ($x = 0$) to an insulating state ($x = 1$) [18]. Another example, the perovskite ANiO_3 ($A = \text{Y, Pr to Lu}$; $n = \infty$), features metal-insulator phase transitions [19–21]. In the solid solution $\text{Nd}_{1-x}\text{A}_x\text{NiO}_3$ ($A = \text{Sm, Eu, Gd, Er, and Yb}$), the metal-insulator transition temperatures can be varied over a large temperature range from 200 to 450 K by substitution of the rare-earth ions [22].

The $A_4\text{Ni}_3\text{O}_{10}$ ($A = \text{La, Pr, Nd}$; $n = 3$), which has recently attracted a lot of interest due its structural similarity to some high- T_c superconductors, shows phase transitions that are accompanied by a resistivity shift at transition temperatures between 128 and 165 K [23–25]. The resistivity of $\text{La}_4\text{Ni}_3\text{O}_{10}$ exhibits an anomaly in both powder and single-crystal samples at $T_{pt} \sim 128$ K, indicating a possible metal-metal phase transition [24,26], which is even more pronounced in $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ [23,25]. In single crystals of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$, even a metal-insulator-like transition is observed along the c axis at $T_{pt} \sim 157$ K [27]. $\text{La}_4\text{Ni}_3\text{O}_{10}$, $\text{Pr}_4\text{Ni}_3\text{O}_{10}$, and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ all show certain changes in their crystal structure at the respective transition temperatures [25,27,28], and different magnetization behaviors between the low-temperature and the high-temperature phases [23,25,27,29].

In this work, we have synthesized solid solution samples of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$) with $x = 0, 1, 2$, and 3 . The successful substitution of La, Pr, and Nd was confirmed by powder x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX). We have performed systematic measurements on their electronic and magnetic properties. These measurements revealed well-defined phase transition temperatures associated with changes of the physical properties for all values of x , some of which are found to be strongly correlated with the Goldschmidt tolerance factor t .

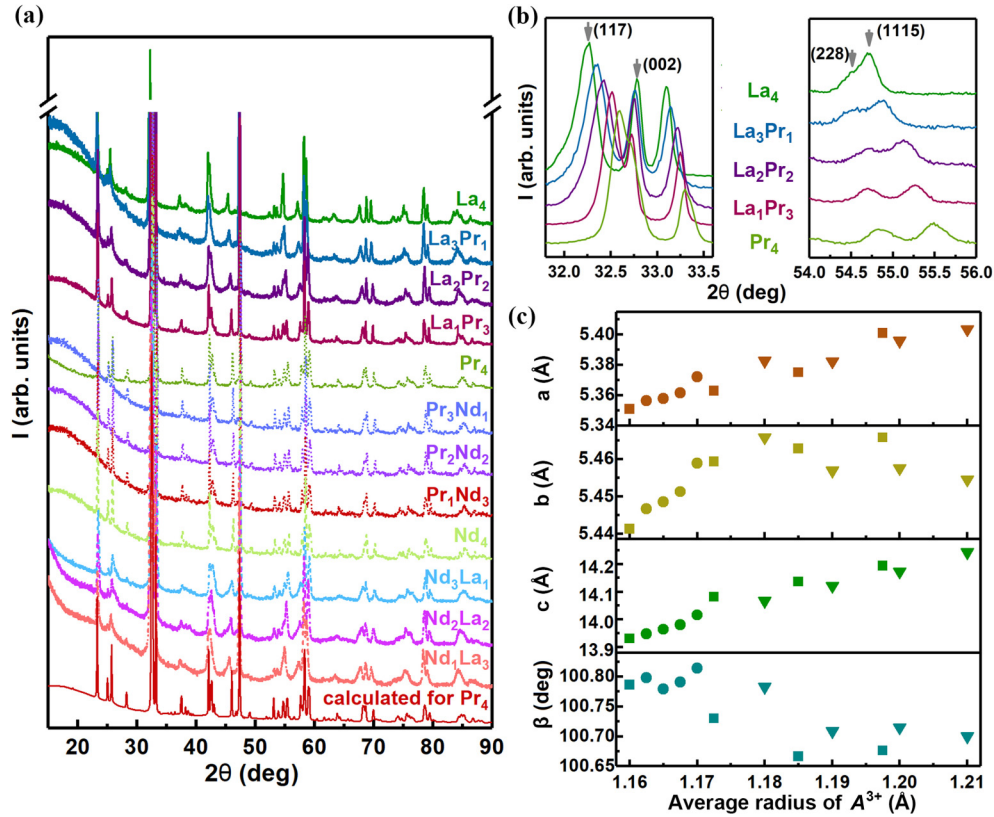


FIG. 1. (a) XRD patterns of the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ samples and calculated pattern from the $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ single-crystal data [27]; solid curves represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), dotted curves $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and dashed curves $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$). (b) Bragg peaks for $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ samples at $2\theta \sim 31.6^\circ$ to $\sim 33.8^\circ$ (left) and at $2\theta \sim 54.0^\circ$ to $\sim 56.0^\circ$ (right), from top to bottom arranged from La to Pr; (c) lattice parameters of the series $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ as functions of the average radius of A^{3+} (B^{3+}), according to the monoclinic space group $P2_1/a$; the triangle, round, and square symbols represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

II. EXPERIMENTAL METHOD

The $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ samples (A and $B = \text{La, Pr, and Nd}$; $x = 0, 1, 2$, and 3) were synthesized via the citrate precursor method [27,30], the details of which are given in Appendix A. These precursors have been annealed at 1100°C in oxygen atmosphere for 24 h, except for $\text{La}_4\text{Ni}_3\text{O}_{10}$ (which does not require oxygen atmosphere) and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ (which needs a reacting time of 72 h). The compacted and pelleted samples for electronic-transport measurements were obtained by pressing the powder and annealing again at 1100°C in oxygen atmosphere for 24 h. All samples were characterized by powder XRD at room temperature [Fig. 1(a)], and the results show sharp peaks without visible impurities. The elemental compositions of all samples were confirmed by EDX (see Appendix C). According to our thermogravimetric analysis, we can confirm an almost stoichiometric oxygen content for all compounds with values around 10.0 within 1% or better (see Table II in Appendix B).

The resistivities of the $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ samples were measured with a physical property measurement system (PPMS, Quantum Design Inc.), and a standard four-probe technique was employed in the temperature range from 10 to 300 K. The magnetic properties were studied by using a Magnetic Properties Measurement System (MPMS 3, Quantum Design Inc.) from 10 to 300 K with an external magnetic field of 0.1 T.

III. RESULTS

As a result of distortions of both shape and arrangement of the NiO_6 octahedra, the crystal structures of the $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ solid solution show a relatively low symmetry. Based on available experimental data, the unit cell of $\text{La}_4\text{Ni}_3\text{O}_{10}$ can be equally well fitted to two types of space groups: $P2_1/a$ (monoclinic) and $Bmab$ (orthorhombic) [28], while the $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ can only be well described by the space group of $P2_1/a$ (monoclinic) [28]. Figure 1(a) shows the powder XRD patterns for all samples involved in this study, and in Fig. 1(c), we summarized all the changes of the corresponding lattice parameters (see Table II in Appendix B). In the $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ series, besides the holistic shift of these patterns that is ascribed to the expansion of unit cells, there are certain specific peak changes as x varies from 0 to 4. In Fig. 1(b), the (117) and (002) peaks ($2\theta \sim 32.5^\circ$) separate gradually as the La content increases, while the (228) and (1115) peaks ($2\theta \sim 54.7^\circ$ and $\sim 55.4^\circ$), on the contrary, gradually merge. A similar tendency is also found for the $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ samples. In the $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ series, however, there is no analogous peak change other than a systematic shift due to the lattice contraction as the Nd content increases. This result is in accordance with the reported space groups [28]. The structural difference between $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{Pr}(\text{Nd})_4\text{Ni}_3\text{O}_{10}$ can be mainly ascribed to the size difference

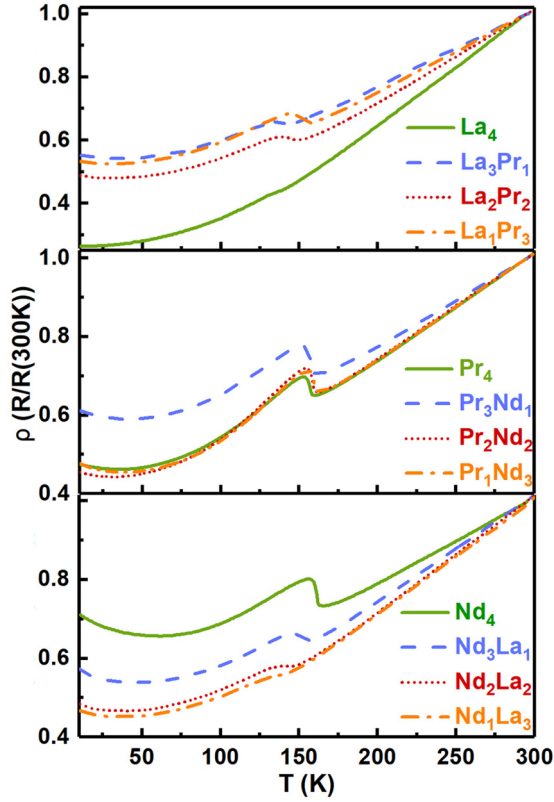


FIG. 2. Zero-field resistivities, normalized to the resistance at 300 K, of the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ as functions of temperature; upper, middle, and bottom show $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

between La^{3+} , Pr^{3+} , and Nd^{3+} , with average radius of 1.21, 1.17, and 1.16 Å in eight and ten coordinations, respectively [31].

To characterize the low-temperature phase transitions at temperatures between 135 and 165 K, we performed electronic-transport measurements on the pelleted samples of the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$. Figure 2 shows the normalized resistivities $\rho(T)/\rho(300\text{ K})$ as a function of temperature from 10 to 300 K. All samples show metallic behaviors in both

the high-temperature and the low-temperature phases, which are consistent with the previous results for the corresponding parent compounds [23]. Besides, we also observe clear anomalies in the resistivity for all compositions at characteristic temperatures T_{pt} , indicating phase transitions with a systematically increasing T_{pt} (from ~ 135 K for $\text{La}_4\text{Ni}_3\text{O}_{10}$ to ~ 157 K for $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and to ~ 161 K for $\text{Nd}_4\text{Ni}_3\text{O}_{10}$) when substituting the rare-earth ions La^{3+} by Pr^{3+} , Pr^{3+} by Nd^{3+} , and La^{3+} by Nd^{3+} , respectively. The associated relative resistivity changes at T_{pt} , $\Delta\rho(T_{pt})/\rho(300\text{ K})$, show a trend to gradually increase from $\sim 2\%$ ($\text{La}_4\text{Ni}_3\text{O}_{10}$) to $\sim 9\%$ ($\text{Pr}_4\text{Ni}_3\text{O}_{10}$) and eventually to $\sim 11\%$ ($\text{Nd}_4\text{Ni}_3\text{O}_{10}$) with decreasing temperature. However, these numbers represent a polycrystalline average and may be affected by the connectivity of the individual grains, and they can therefore not represent the intrinsic anisotropic values obtained on single crystals [27].

We also measured the magnetization for the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ at temperatures between 10 and 300 K [Fig. 3(a)] to characterize the changes in the magnetic properties as functions of their $A(B)$ constituents. The magnetic-susceptibility data of the zero-field cooling (ZFC) and the field cooling (FC) essentially overlap within the measured temperature range. The magnetic susceptibility of $\text{La}_4\text{Ni}_3\text{O}_{10}$ decreases with the decreasing temperature in the high-temperature phase, while in the low-temperature phase, the susceptibility increases as the temperature decreases, which is similar to previous reports [23,29]. None of the phases follows a single simple Curie-Weiss law over the whole temperature range. However, except for $\text{La}_4\text{Ni}_3\text{O}_{10}$, the temperature dependence of the magnetic susceptibilities $\chi(T)$ of all the other compositions in the $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ series can be well fitted by a Néel type of Curie-Weiss law for the high-temperature phase, $\chi(T) = \frac{C}{T+\Theta} + \chi_0$, demonstrating a paramagnetic behavior at these temperatures. The temperature window used for this fitting procedure was chosen between $T_{pt} + 15$ and 300 K. The corresponding results are listed in Table I and shown in Fig. 4. If we take the magnetic-susceptibility data of $\text{La}_4\text{Ni}_3\text{O}_{10}$ as a measure for possible Ni-containing paramagnetic impurities, we obtain in the worst case a contribution of $\approx 0.01\text{ emu K Oe}^{-1}\text{ mol}^{-1}$ to the listed values of C (see the Appendix E). Apart from the changes in $\chi(T)$ at T_{pt} , we have no indications for further magnetic transitions in the whole investigated temperature range.

TABLE I. Fitting results of the $\chi(T)$ data and phase transition temperatures of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$; $x = 0, 1, 2, 3$).

	$C(\text{emu K Oe}^{-1}\text{ mol}^{-1})$	$\chi_0(\text{emu Oe}^{-1}\text{ mol}^{-1})$	$\theta(\text{K})$	t	$T_{pt}(\text{K})$
$\text{La}_4\text{Ni}_3\text{O}_{10}$ ^a	—	$2.4(1) \times 10^{-3}$	—	0.9140	135.5
$\text{La}_3\text{Pr}_1\text{Ni}_3\text{O}_{10}$	1.88(3)	$1.6(1) \times 10^{-3}$	50(2)	0.9107	139.5
$\text{La}_2\text{Pr}_2\text{Ni}_3\text{O}_{10}$	4.00(9)	$1.3(3) \times 10^{-3}$	50(3)	0.9071	144.0
$\text{La}_1\text{Pr}_3\text{Ni}_3\text{O}_{10}$	5.75(2)	$2.1(4) \times 10^{-3}$	51(4)	0.9036	151.0
$\text{Pr}_4\text{Ni}_3\text{O}_{10}$	7.6(3)	$7(4) \times 10^{-4}$	51(4)	0.9000	157.0
$\text{Pr}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$	7.6(3)	$1.5(4) \times 10^{-3}$	55(4)	0.8991	157.8
$\text{Pr}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$	7.6(2)	$1.7(4) \times 10^{-3}$	55(3)	0.8982	158.8
$\text{Pr}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$	7.6(3)	$1.8(5) \times 10^{-3}$	52(4)	0.8973	159.6
$\text{Nd}_4\text{Ni}_3\text{O}_{10}$	7.7(3)	$2.9(6) \times 10^{-3}$	61(5)	0.8964	160.5
$\text{La}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$	5.2(2)	$3.6(4) \times 10^{-3}$	46(4)	0.9009	150.0
$\text{La}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$	3.5(2)	$3.2(4) \times 10^{-3}$	44(7)	0.9053	142.0
$\text{La}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$	1.74(4)	$1.7(1) \times 10^{-3}$	54(3)	0.9098	136.5

^aThe Pauli-paramagnetic susceptibilities of $\text{La}_4\text{Ni}_3\text{O}_{10}$ are estimated directly from the measured data right below 300 K.

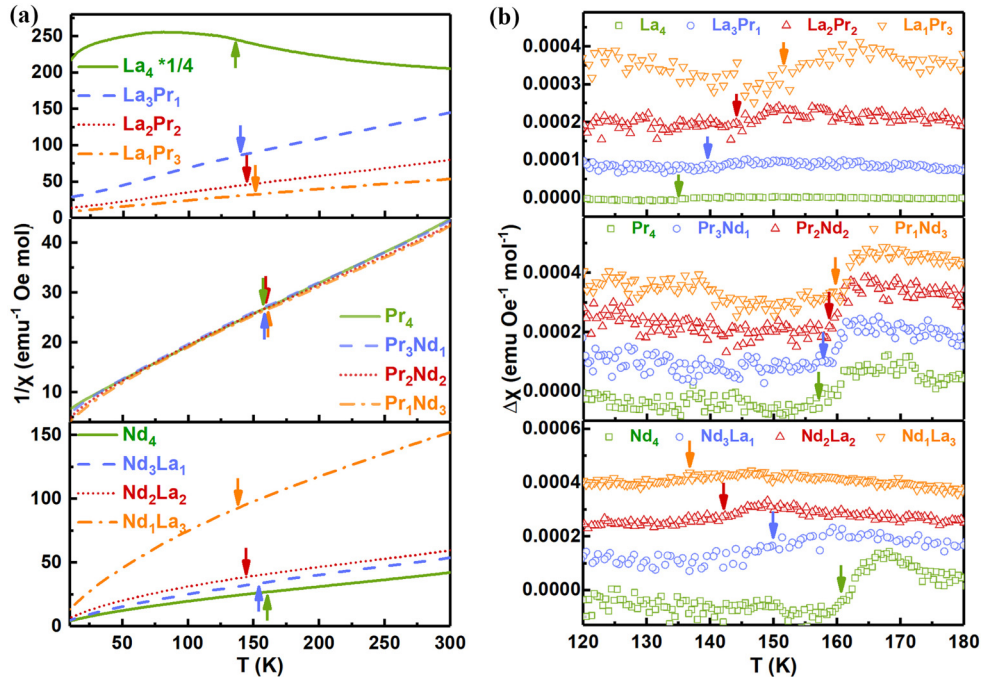


FIG. 3. (a) $1/\chi$ of the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ as functions of temperature; the data for $\text{La}_4\text{Ni}_3\text{O}_{10}$ are multiplied by 1/4 for clarity; (b) The same $\chi(T)$ data after subtraction of a fitted Curie-Weiss background (third-order polynomial background for $\text{La}_4\text{Ni}_3\text{O}_{10}$) in a temperature window of ± 50 K around the respective T_{pt} (marked with arrows); the data are offset by 0.000 12 emu Oe⁻¹ mol⁻¹ for clarity; upper, middle, and bottom show $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

IV. DISCUSSION

The Goldschmidt tolerance factor t is widely used to estimate the stability of the rare-earth perovskitelike structures, with $t = (r_{\text{rare-earth}} + r_{\text{O}})/\sqrt{2}(r_{\text{Ni}} + r_{\text{O}})$ [32], where $r_{\text{rare earth}}$, r_{Ni} , and r_{O} represent the average ionic radius of the rare-earth, nickel, and oxygen ions in the corresponding coordinations, respectively. It is found that the values of t in the RP type of compounds range from 0.86 to 0.99 [20,33,34]. By linear interpolation of the reported ionic radius [31,35], the t for all the samples of the solid solution $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ can be estimated. Upon changing $A^{3+}(B^{3+})$, from La^{3+} with the largest ionic radius, to Nd^{3+} with the smallest ionic radius, the tolerance factor t decreases from 0.914 to 0.896 (Fig. 5). Considering our experience in the syntheses of these compounds, it becomes more and more difficult to obtain $A_4\text{Ni}_3\text{O}_{10}$ as $A^{3+}(B^{3+})$ changes from La^{3+} to Pr^{3+} (Nd^{3+}), and from Pr^{3+} to Nd^{3+} , suggesting that a larger value of t results in a more stable phase. The t difference between $\text{La}_4\text{Ni}_3\text{O}_{10}$ (0.914) and $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ (0.900) is larger than that between $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ (0.900) and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ (0.896). In any case, we can expect that the structures of these compounds gradually change with t , which in turn should lead to a certain t dependence of the physical properties in connection with the phase transition.

Figure 6 shows the corresponding transition temperatures T_{pt} and the absolute resistivities $\rho(300\text{ K})$ as functions of t . The T_{pt} values were obtained from the peaks in $d\rho/dT$, as $\rho(T)$ discontinuously changes at the phase transition (see Fig. 2) [25,27]. Except for $\text{La}_4\text{Ni}_3\text{O}_{10}$ without obvious shift of $\chi(T)$ at T_{pt} , corresponding T_{pt} data taken from $\chi(T)$ are consistent with the $\rho(T)$ results within ± 0.5 K. As shown in Fig. 6(a), T_{pt} is found to almost linearly decrease with t ,

with a slope of $dT_{pt}/dt \sim 1.6 \times 10^3$ K. Although the t dependence of transition temperature T_{pt} is similar to ANiO_3 , the slope dT_{pt}/dt of $A_4\text{Ni}_3\text{O}_{10}$ is approximately ten times smaller than that in ANiO_3 [20]. Similarly, the absolute values of the resistivity at room temperature [Fig. 6(b)] systematically decrease with t . Generally, for $t = 1$, the distortion of the NiO_6 octahedra is known to be minimum [33], the Ni-O-Ni angles are close to 180° , and the overlap between the Ni d orbitals and the O p orbitals is maximized. This may explain the increasing metallicity in $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ with t in a similar way as it has been reported to be the case for ANiO_3 [20].

For most compositions, there is a steplike decrease $\Delta\chi$ of $\chi(T)$ at T_{pt} with decreasing temperature, as we illustrate it in Fig. 3(b). The same behavior has also been observed in $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ powders [25], and we had interpreted this feature for $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ single crystals in terms of a first-order phase transition [27]. As the entropy change ΔS , the $\Delta\chi$, and the slope of the field-dependent $T_{pt}(B)$ are not independent from each other at such transitions, the sign of $\Delta\chi$ dictates the sign of dT_{pt}/dB and vice versa [27], indicating a slight suppression of T_{pt} with magnetic field in all cases, although its expected magnitude (≈ 50 mK in $B = 7$ T for $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ [27]) is beyond the temperature resolution of our present data.

The Pauli-paramagnetic susceptibilities obtained from our Curie-Weiss type fits [Figs. 4(b) and 19(b)] do not show any clear trend and scatter around $\chi_0 \sim 2 \times 10^{-3}$ emu Oe⁻¹ mol⁻¹, but are an order of magnitude larger than the free-electron value $\chi_0^{f.e} \sim 10^{-4}$ emu Oe⁻¹ mol⁻¹ [27].

The corresponding Curie constants C show, as expected, large variations depending on the amount and the species of the rare-earth ions [Figs. 4(a) and 19(a)]. However, we

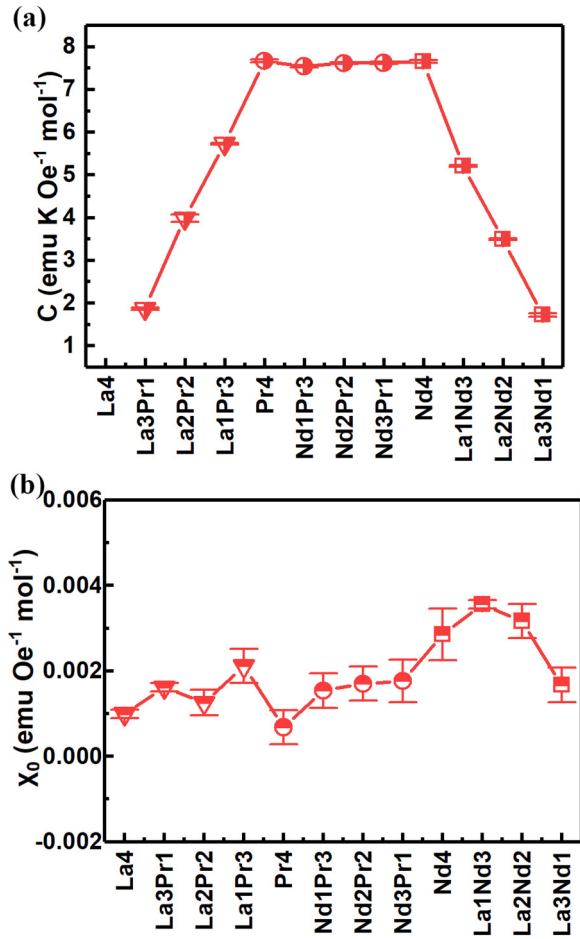


FIG. 4. Curie constants C (a) and Pauli-paramagnetic susceptibilities χ_0 (b) as functions of element contents, calculated from the magnetic susceptibilities of the high-temperature phase; the triangle, round, and square symbols represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

observe systematically larger C values than expected from a free-ion picture, namely, $\approx 7.6\text{--}7.7\text{ emu K Oe}^{-1}\text{ mol}^{-1}$ for the end members $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$, corresponding to $\approx 3.9\ \mu_B$ per rare-earth ion, which has to be compared to the expected values $\approx 3.58\ \mu_B$ for $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and $\approx 3.62\ \mu_B$ for $\text{Nd}_4\text{Ni}_3\text{O}_{10}$, respectively. As our nonmagnetic $\text{La}_4\text{Ni}_3\text{O}_{10}$ samples prepared by similar methods do not show any sign of localized magnetic moments in the magnetic susceptibility (contributing to less than $0.01\text{ emu K Oe}^{-1}\text{ mol}^{-1}$, see Appendix E), and a similarly large Curie constant was found in single-crystalline $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ prepared by different methods [27], we suggest that these values may be intrinsic and are not due to Ni-containing impurities. Larger-than-expected measured magnetic moments in rare-earth oxides have been reported for Nd_2WO_6 ($\approx 4.36\ \mu_B$) [36], but also (and more important in the present context) for the $n = 1$ members of the RP nickelates Pr_2NiO_4 and Nd_2NiO_4 , with magnetic moments up to $\approx 4.0\ \mu_B$ for Pr_2NiO_4 [37] and $\approx 4.8\ \mu_B$ for Nd_2NiO_4 [38], which had been attributed to interaction effects between the rare-earth and the Ni ions. On the other hand, the only systematic report on $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ that we are aware of (with C

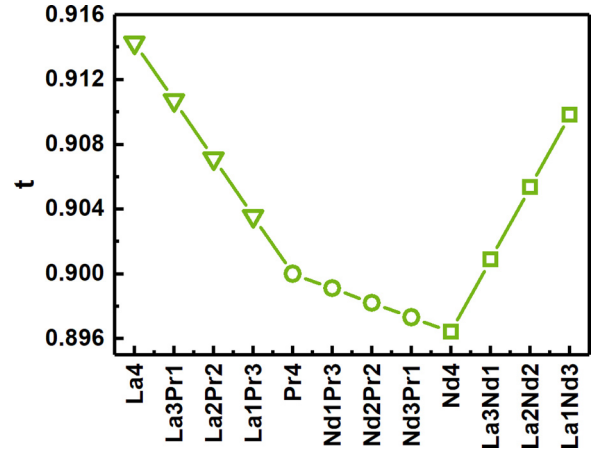


FIG. 5. Tolerance factor t of the solid solution $\text{A}_{4-x}\text{B}_x\text{Ni}_3\text{O}_{10}$ as a function of element content; the triangle, round, and square symbols represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

$\approx 6.4\text{ emu K Oe}^{-1}\text{ mol}^{-1}$ [25]) does not at all seem to support our observation. However, we would like to mention that the oxygen contents of our $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ samples (≈ 9.93) are closer to the ideal value 10.00 (see Table II in Appendix B) and differ from those reported in Ref. [25] (≈ 9.85) for samples prepared by a different synthesis technique, which may have implications on the magnetic behavior. Within this line of arguments, we also expect that the number of delocalized electrons due to the mixed valent $\text{Ni}^{2+/3+}$ is very sensitive to the exact oxygen content. As the number of such charge carriers is closely related to the Pauli-spin susceptibility via the electron density of states, it is plausible that our value for χ in $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ ($\approx 2.9 \times 10^{-3}\text{ emu Oe}^{-1}\text{ mol}^{-1}$) differs from that reported in Ref. [25] ($\approx 4.4 \times 10^{-3}\text{ emu Oe}^{-1}\text{ mol}^{-1}$).

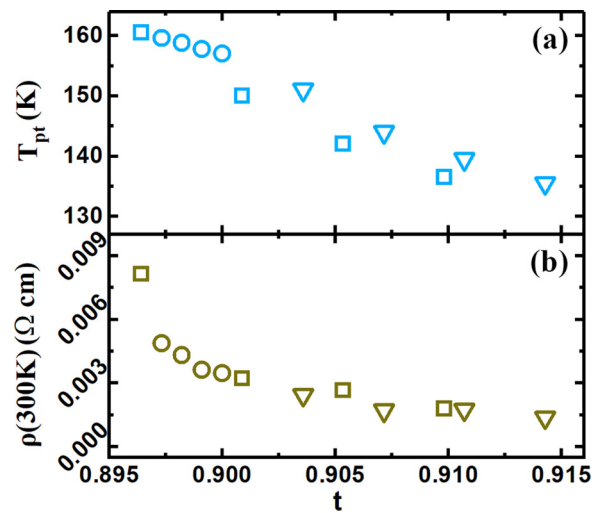


FIG. 6. Tolerance factor dependence of the phase transition temperatures T_{pt} (a), the estimated absolute value of the resistivity at 300 K (b); the triangle, round, and square symbols represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively; the error in $\rho(300\text{ K})$ due to the contact geometry is $\sim 30\%$.

Finally, we state that all the data given in Table I and shown in the figures were obtained on pressed powders; i.e., they represent polycrystalline averages. Nevertheless, the quantitative and qualitative agreement of our data obtained for $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ powders with those measured in $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ single crystals [27] suggests that the trends described here reflect those of intrinsic properties of the whole series $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$.

V. CONCLUSION

We have successfully synthesized a series of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$) compounds via the citrate precursor method in different reacting atmospheres. The phase transition temperatures T_{pt} and the room-temperature resistivities $\rho(300\text{ K})$ vary systematically with the Goldschmidt tolerance factor t , and may even possibly be controlled by it. With increasing t , the compounds become more conducting, which we may attribute to a successively diminishing distortion of the NiO_6 octahedra which are responsible for the electron transport in these materials. Our results indicate that, while the associated changes of the Ni-O bond lengths and Ni-O-Ni bond angles play a crucial role for the electronic structure of these compounds, the magnetism of the $A^{3+}(B^{3+})$ ions upon replacing La by Pr or Nd is not a decisive factor.

ACKNOWLEDGMENT

This work was supported by the Swiss National Science Foundation under Grant No. 20-175554.

APPENDIX A: SYNTHESIS

Powdered samples of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr}$ and Nd ; $x = 0, 1, 2, 3$) were synthesized by a citric acid assisted sol-gel method. The reactants La_2O_3 (99.9%; Sigma-Aldrich), Pr_6O_{11} (99.9%; Sigma-Aldrich), Nd_2O_3 (99.9%; Fluka Chemical), and NiO (99.99%; Sigma-Aldrich) were weighted in stoichiometric ratios. Then, nitric acid (65% for analysis; Emsure) was used for dissolving these oxides, and a clear green liquid was obtained. After adding citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$; 99.5%; Emsure) in a molar ratio 1:1 with respect to the molar contents of cations, the

resulting liquid was heated at around 300°C on a heating plate, dried, and decomposed into a dark brown powder. Finally, an ultrafine and homogeneous powder of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ was obtained by annealing the precursor powder at 1100°C in flowing oxygen for 24 h, except for $\text{La}_4\text{Ni}_3\text{O}_{10}$ (which does not require oxygen atmosphere) and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ (which needs a reacting time of 72 h). The compacted pelleted samples were obtained by pressing the powder and annealing again at 1100°C in oxygen atmosphere for another 24 h.

The oxygen contents of the obtained compounds were determined by thermogravimetric reduction with 10% of H_2/N_2 gas, and the corresponding results are shown in Table II.

APPENDIX B: POWDER X-RAY DIFFRACTION

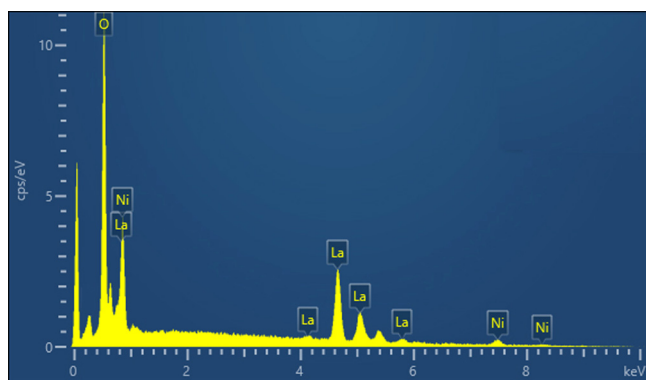
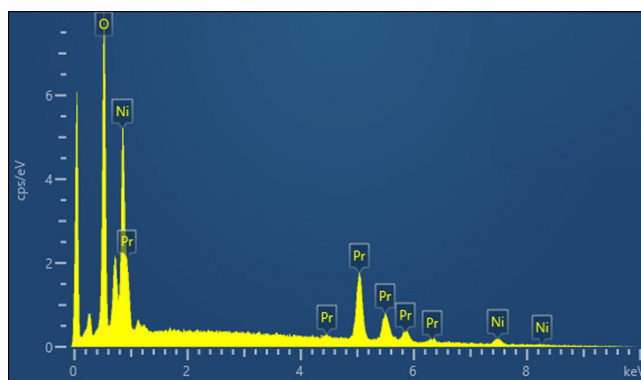
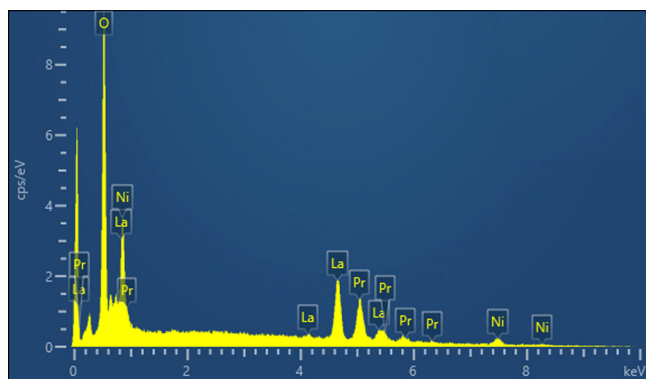
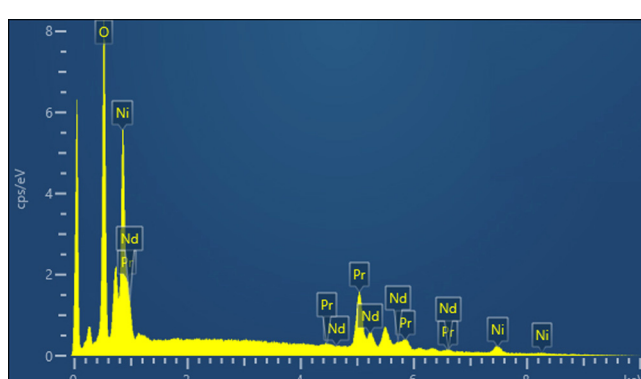
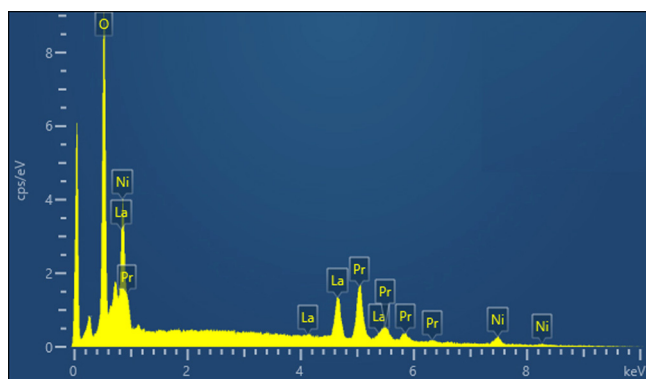
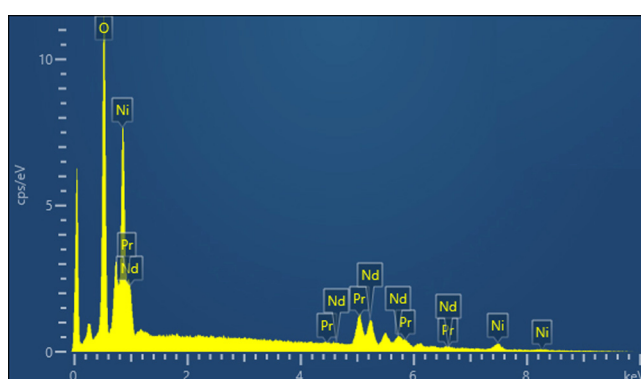
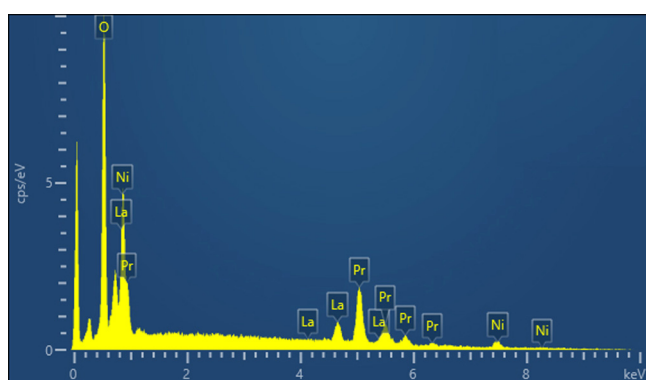
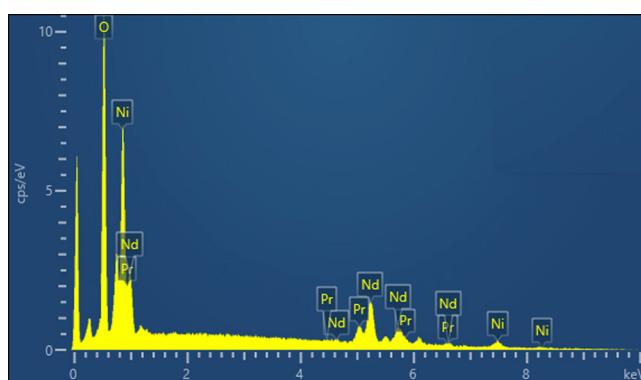
Powder x-ray diffraction (PXRD) data were collected at room temperature in transmission mode using a Stoe Stadi P diffractometer equipped with a $\text{Cu K}\alpha_1$ radiation [$\text{Ge}(111)$] monochromator and a Dectris Mythen 1K detector. The reflections of the main phase were indexed with a monoclinic cell in the space group $P2_1/a$ (No. 14). The Rietveld refinement analysis [39] of the diffraction patterns was performed with the FULLPROF SUITE package [40,41] (version March 2019). The structural model was taken from the single-crystal x-ray diffraction refinement. Refined parameters were scale factor, zero shift, transparency, lattice parameters, Pr and Ni atomic positions, and peak shapes as a Thompson-Cox-Hastings pseudo-Voigt function. A preferred orientation correction as a modified March function was implemented in the analysis. The refinement data are listed in Table II.

APPENDIX C: ENERGY-DISPERSIVE X-RAY SPECTROSCOPY

The elemental compositions are determined by means of energy-dispersive x-ray (EDX) analysis integrated into the Zeiss Supra 50 VP scanning electron microscope (SEM). The data taken on all the compacted samples of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ confirmed the presence of La, Pr, and Nd with element contents that are in very good agreement with the expected ratios (see Figs. 7–18 and Tables III–XIV).

TABLE II. Crystallographic parameters obtained from the Rietveld refinements of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ (A and $B = \text{La, Pr, and Nd}$; $x = 0, 1, 2, 3$) at room temperature as well as their oxygen contents as determined from thermogravimetric measurements.

	a (Å)	b (Å)	c (Å)	β (deg)	$R_p(\%)$	$R_{wp}(\%)$	χ^2	O content
$\text{La}_4\text{Ni}_3\text{O}_{10}$	5.403	5.454	14.24	100.70	4.89	9.08	12.6	10.03
$\text{La}_3\text{Pr}_1\text{Ni}_3\text{O}_{10}$	5.396	5.458	14.17	100.71	2.69	4.27	3.01	10.10
$\text{La}_2\text{Pr}_2\text{Ni}_3\text{O}_{10}$	5.382	5.457	14.12	100.71	3.19	5.27	4.71	10.01
$\text{La}_1\text{Pr}_3\text{Ni}_3\text{O}_{10}$	5.382	5.466	14.07	100.78	2.56	4.15	5.14	10.00
$\text{Pr}_4\text{Ni}_3\text{O}_{10}$	5.372	5.458	14.02	100.81	2.32	3.59	5.28	9.97
$\text{Pr}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$	5.361	5.451	13.98	100.79	2.18	3.27	2.10	9.95
$\text{Pr}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$	5.358	5.449	13.96	100.78	2.35	3.63	2.45	9.93
$\text{Pr}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$	5.356	5.447	13.95	100.80	2.19	3.26	1.94	10.07
$\text{Nd}_4\text{Ni}_3\text{O}_{10}$	5.351	5.441	13.93	100.79	2.52	3.85	2.67	9.93
$\text{La}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$	5.363	5.459	14.08	100.73	5.33	9.14	9.66	9.98
$\text{La}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$	5.375	5.463	14.14	100.67	5.67	10.0	13.8	9.99
$\text{La}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$	5.401	5.466	14.19	100.68	4.14	6.94	8.01	9.95

FIG. 7. EDX spectrum of $\text{La}_4\text{Ni}_3\text{O}_{10}$.FIG. 11. EDX spectrum of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$.FIG. 8. EDX spectrum of $\text{La}_3\text{Pr}_1\text{Ni}_3\text{O}_{10}$.FIG. 12. EDX spectrum of $\text{Pr}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$.FIG. 9. EDX spectrum of $\text{La}_2\text{Pr}_2\text{Ni}_3\text{O}_{10}$.FIG. 13. EDX spectrum of $\text{Pr}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$.FIG. 10. EDX spectrum of $\text{La}_1\text{Pr}_3\text{Ni}_3\text{O}_{10}$.FIG. 14. EDX spectrum of $\text{Pr}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$.

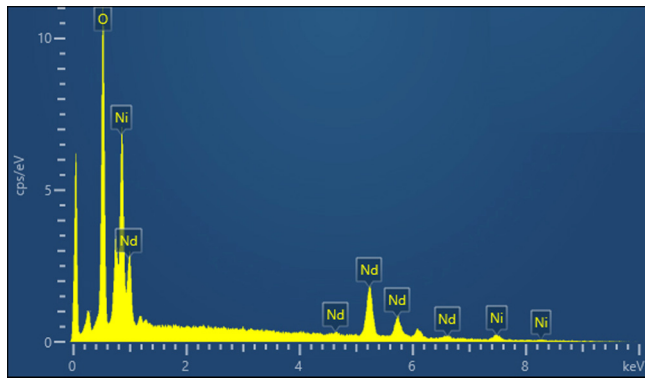
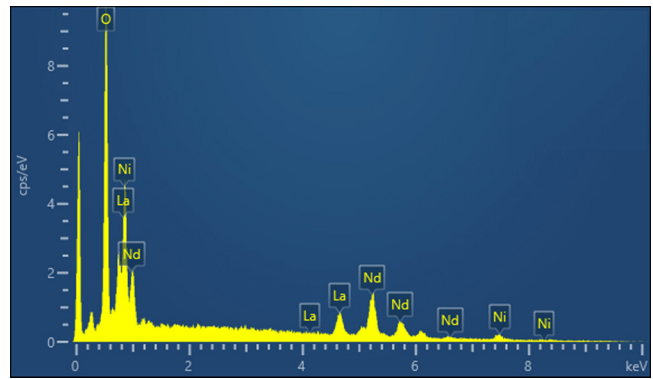
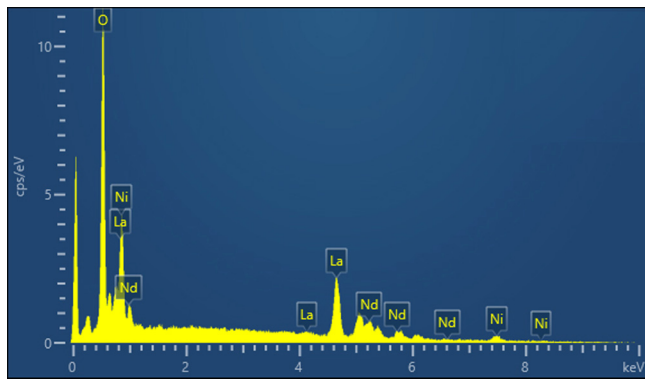
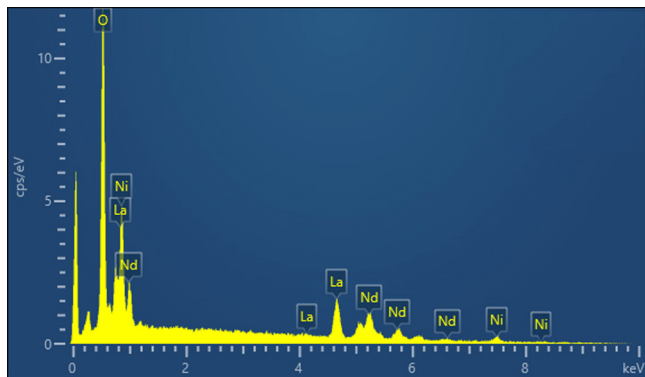
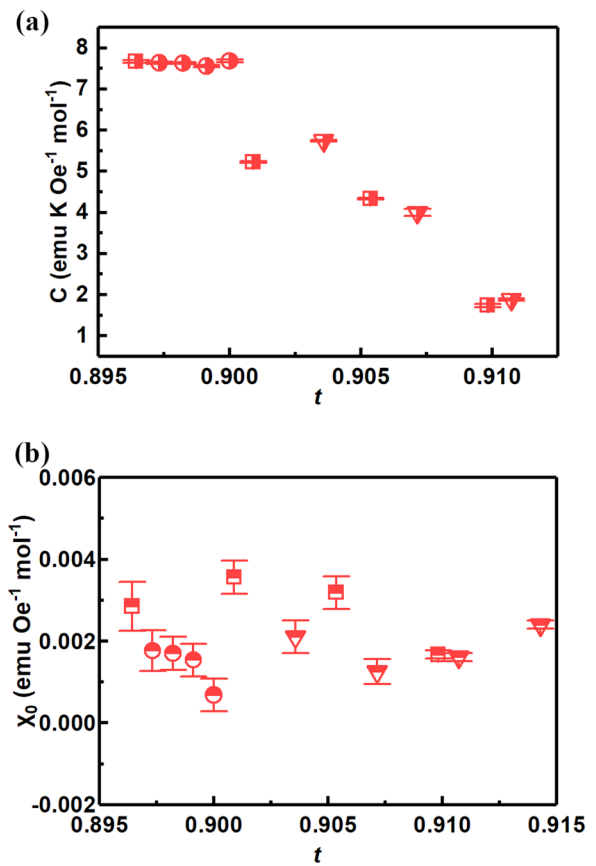

 FIG. 15. EDX spectrum of $\text{Nd}_4\text{Ni}_3\text{O}_{10}$.

 FIG. 18. EDX spectrum of $\text{La}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$.

 FIG. 16. EDX spectrum of $\text{La}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$.

 FIG. 17. EDX spectrum of $\text{La}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$.


FIG. 19. Curie constants C (a) and Pauli-paramagnetic susceptibilities χ_0 (b) as functions of tolerance factor t , calculated from the magnetic susceptibilities of the high-temperature phase; the triangle, round, and square symbols represent $\text{La}_{4-x}\text{Pr}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), $\text{Pr}_{4-x}\text{Nd}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), and $\text{Nd}_{4-x}\text{La}_x\text{Ni}_3\text{O}_{10}$ ($x = 0, 1, 2, 3$), respectively.

TABLE III. Element contents of $\text{La}_4\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
La	63.5	25.0	La	64.1	25.4	La	63.2	24.8
Ni	20.1	18.7	Ni	19.5	18.3	Ni	20.4	18.9
O	26.1	56.3	O	16.4	56.3	O	16.5	56.2
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of La/Ni:4.01(6)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
La	63.5	25.0	La	63.3	24.9			
Ni	20.1	18.7	Ni	20.3	18.9			
O	16.4	56.3	O	16.5	56.2			
Total	100		Total	100				

TABLE IV. Element contents of $\text{La}_3\text{Pr}_1\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	16.1	6.2	Pr	17.2	6.7	Pr	16.6	6.4
La	46.4	18.2	La	47.0	18.6	La	46.4	18.3
Ni	21	19.5	Ni	19.5	18.3	Ni	20.6	19.2
O	16.1	56.1	O	16.4	56.3	O	16.4	56.2
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ La/Ni:1.01(4)/2.84(9)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	17	6.6	Pr	16.8	6.5			
La	45.5	17.8	La	45.8	17.9			
Ni	21.1	19.5	Ni	21.1	19.5			
O	16.5	5.1	O	16.5	56.1			
Total	100		Total	100				

TABLE V. Element contents of $\text{La}_2\text{Pr}_2\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	33.9	13.3	Pr	33.7	13.1	Pr	34.1	13.3
La	29.8	11.8	La	29.4	11.6	La	29.8	11.8
Ni	19.9	18.6	Ni	20.4	19.1	Ni	29.8	18.5
O	16.4	56.3	O	16.4	56.2	O	16.3	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ La/Ni:2.11(6)/1.87(6)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	33.9	13.1	Pr	34.2	13.4			
La	28.9	11.4	La	29.9	11.9			
Ni	20.8	19.3	Ni	19.6	18.4			
O	16.4	26.1	O	16.3	56.3			
Total	100		Total	100				

TABLE VI. Element contents of $\text{La}_1\text{Pr}_3\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	48.4	18.8	Pr	49.1	19.2	Pr	48.1	18.7
La	14.6	5.8	La	14.3	5.7	La	14.7	5.8
Ni	20.6	19.3	Ni	20.1	18.9	Ni	20.8	19.4
O	16.4	56.1	O	16.3	56.2	O	16.4	56.1
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ La/Ni:2.95(6)/0.91(2)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	48.7	19.0	Pr	47.7	18.6			
La	14.5	5.8	La	15.4	6.1			
Ni	20.4	19.1	Ni	20.5	19.2			
O	16.4	56.2	O	16.4	56.2			
Total	100		Total	100				

TABLE VII. Element contents of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	63.5	24.8	Pr	63.8	25	Pr	64	25.1
Ni	20.2	19.0	Ni	20.0	18.8	Ni	19.7	18.6
O	16.3	56.2	O	16.3	56.2	O	16.3	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/Ni: 4.01(5)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	64.2	25.2	Pr	63.9	25.1			
Ni	19.6	18.5	Ni	19.8	18.7			
O	16.3	56.3	O	16.3	56.3			
Total	100		Total	100				

TABLE VIII. Element contents of $\text{Pr}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	48	18.9	Pr	48.1	18.9	Pr	49.1	19.4
Nd	15.7	6.0	Nd	15.4	6.0	Nd	15.3	5.9
Ni	20.0	18.9	Ni	20.0	18.8	Ni	19.4	18.4
O	16.2	56.2	O	16.2	56.2	O	16.2	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ Nd/Ni:3.00(8)/0.96(1)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	47.2	18.5	Pr	47.1	18.5			
Nd	16.2	6.2	Nd	16.3	6.2			
Ni	20.4	19.2	Ni	20.1	19.1			
O	16.3	56.2	O	16.3	56.2			
Total	100		Total	100				

TABLE IX. Element contents of $\text{Pr}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	31.8	12.5	Pr	32.0	12.7	Pr	32.3	12.3
Nd	32.0	12.3	Nd	32.1	12.4	Nd	31.9	12.8
Ni	20.0	18.9	Ni	19.7	18.7	Ni	19.6	18.6
O	16.2	56.2	O	16.2	56.3	O	16.2	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ Nd/Ni: 1.97(5)/1.97(5)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	31.1	12.2	Pr	31.6	12.4			
Nd	32.2	12.4	Nd	31.7	12.2			
Ni	20.4	19.3	Ni	20.5	19.3			
O	16.2	56.1	O	16.2	56.1			
Total	100		Total	100				

TABLE X. Element contents of $\text{Pr}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Pr	15.8	6.4	Pr	16.7	6.2	Pr	16.7	6.6
Nd	47.8	19.0	Nd	48.1	19.2	Nd	47.6	18.6
Ni	20.3	18.4	Ni	19.2	18.4	Ni	19.6	18.4
O	16.2	56.2	O	16.1	56.2	O	16.1	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Pr/ Nd/Ni: 1.02(3)/3.08(4)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Pr	15.7	6.2	Pr	15.4	6.1			
Nd	48.2	18.9	Nd	48.1	19.2			
Ni	20.0	18.6	Ni	20.3	18.5			
O	16.1	56.2	O	16.2	56.2			
Total	100		Total	100				

TABLE XI. Element contents of $\text{Nd}_4\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
Nd	64.3	25.0	Nd	64.8	25.3	Nd	64.3	25.0
Ni	19.7	18.8	Ni	19.2	18.4	Ni	19.7	18.8
O	16.1	56.2	O	16.0	56.3	O	16.1	56.2
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of Nd/Ni: 4.04(6)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
Nd	64.6	25.2	Nd	64.4	25.0			
Ni	19.4	18.5	Ni	19.6	18.7			
O	16.0	56.3	O	16.0	56.3			
Total	100		Total	100				

TABLE XII. Element contents of $\text{La}_3\text{Nd}_1\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
La	47.0	18.6	La	46.1	17.9	La	45.5	18.9
Nd	16.9	6.5	Nd	16.9	6.9	Nd	16.1	16.7
Ni	19.8	18.7	Ni	20.5	18.9	Ni	22.0	18.1
O	16.3	56.2	O	16.5	56.3	O	16.4	56.3
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of La/Nd/Ni: 2.9(1)/1.04(5)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
La	45.1	18.4	La	46.0	18.1			
Nd	18.5	16.3	Nd	16.5	6.3			
Ni	20.0	19.1	Ni	21.2	19.4			
O	16.4	56.2	O	16.3	56.2			
Total	100		Total	100				

TABLE XIII. Element contents of $\text{La}_2\text{Nd}_2\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
La	30.5	12.2	La	30.0	11.9	La	31.1	12.6
Nd	33.0	12.6	Nd	33.0	12.6	Nd	33.4	13.0
Ni	20.1	19.0	Ni	20.7	19.3	Ni	19.2	18.2
O	16.4	56.3	O	16.3	56.2	O	16.3	56.2
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of La/Nd/Ni: 1.95(6)/2.01(5)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
La	31.2	12.4	La	30.4	12.1			
Nd	32.3	12.5	Nd	32.7	12.5			
Ni	20.1	18.8	Ni	20.5	19.1			
O	16.4	56.3	O	16.4	56.3			
Total	100		Total	100				

TABLE XIV. Element contents of $\text{La}_1\text{Nd}_3\text{Ni}_3\text{O}_{10}$.

Point 1			Point 2			Point 3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %	Element	Weight %	Atomic %
La	15.1	6.1	La	14.9	6.0	La	15.1	6.1
Nd	49.5	19.2	Nd	49.9	19.4	Nd	19.2	19.1
Ni	19.3	18.4	Ni	19.1	18.2	Ni	19.6	18.7
O	16.1	56.3	O	16.1	56.4	O	16.1	56.2
Total	100		Total	100		Total	100	
Point 4			Point 5			Average rate of La/Nd/Ni: 0.98(3)/3.0(1)/3		
Element	Weight %	Atomic %	Element	Weight %	Atomic %			
La	15.1	5.9	La	16.2	6.5			
Nd	49.5	18.4	Nd	48.1	18.6			
Ni	19.3	19.6	Ni	19.5	18.5			
O	16.1	56.1	O	16.2	56.3			
Total	100		Total	100				

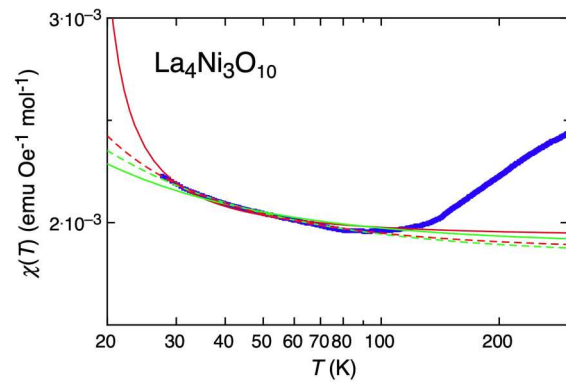
APPENDIX D: PHYSICAL PROPERTY MEASUREMENTS

The resistivity measurements of the $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ pelleted samples were performed in a Physical Property Measurement System (PPMS, Quantum Design Inc.), and a standard four-probe technique was employed with 50- μm silver wires attached with silver paint. All the measurements were performed with an applied current of $I = 0.5\text{ mA}$ in the temperature range from 10 to 300 K.

The magnetic properties of $A_{4-x}B_x\text{Ni}_3\text{O}_{10}$ were studied with a Magnetic Properties Measurement System (MPMS 3, Quantum Design Inc.). In the temperature dependent magnetization $[M(T)]$ measurements, both zero-field cooling and field cooling processes were measured in the temperature range of 10 to 300 K with an external magnetic field of 0.1 T. The corresponding fitted results of a Néel type of Curie-Weiss law are shown in Figs. 4 and 19.

APPENDIX E: ESTIMATION OF POSSIBLE MAGNETIC IMPURITIES DUE TO Ni

According to our x-ray data, we could not identify any impurity phases. To obtain an estimate of an upper bound of contributions to the magnetic susceptibility due to Ni-containing impurities, we refer here to the $\chi(T)$ data of $\text{La}_4\text{Ni}_3\text{O}_{10}$ where a significant contribution due to Ni impurities should be most visible. We performed various fits (see Fig. 20), and obtain in the worst scenario a contribution to $C \approx 0.01\text{ emu K Oe}^{-1}\text{ mol}^{-1}$ at low temperatures, corresponding to $0.025 \approx \text{spin-}\frac{1}{2}$ or $\approx 0.008\text{ spin-1}$ magnetic moments per formula unit. Considering the identical preparation conditions for all samples and assuming similar contamination levels, we can state that the values for C ranging between ≈ 1.2 and $7.7\text{ emu Oe}^{-1}\text{ mol}^{-1}$ are hardly affected by possible Ni impurities.



$\chi(T) = C/(T+\Theta) + \chi_0$	$C = 3.14 \times 10^{-3}$	$\Delta C = 2.53 \cdot 4$
	$\Theta = -17.6$	$\Delta \Theta = 0.93$
Fitting range 25K - 140 K	$\chi_0 = 1.94 \times 10^{-3}$	$\Delta \chi_0 = 3.66 \times 10^{-6}$
$\chi(T) = C/T + \chi_0$	$C = 7.65 \times 10^{-3}$	$\Delta C = 2.33 \cdot 4$
Fitting range 25K - 100 K	$\Theta = -6.27$	$\Delta \Theta = 0.59$
	$\chi_0 = 1.87 \times 10^{-3}$	$\Delta \chi_0 = 2.62 \times 10^{-6}$
$\chi(T) = C/T + \chi_0$	$C = 7.83 \times 10^{-3}$	$\Delta C = 2.35 \cdot 4$
Fitting range 25K - 140 K	$\chi_0 = 1.90 \times 10^{-3}$	$\Delta \chi_0 = 3.80 \times 10^{-6}$
$\chi(T) = C/T + \chi_0$	$C = 1.02 \times 10^{-2}$	$\Delta C = 7.3 \times 10^{-5}$
Fitting range 25K - 100 K	$\chi_0 = 1.84 \times 10^{-3}$	$\Delta \chi_0 = 1.39 \times 10^{-6}$

FIG. 20. Results from various Curie-Weiss-like fits to the magnetic susceptibility of $\text{La}_4\text{Ni}_3\text{O}_{10}$ to estimate the contribution of magnetic impurities.

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